

PATENT ABSTRACTS OF JAPAN

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(71)Applicant : ONKYO CORP

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(54) MEMBER FOR LOUDSPEAKER AND ITS MANUFACTURE

(57)Abstract:

PROBLEM TO BE SOLVED: To produce no poisonous gas at smoking, to make a member lightweight and high in elasticity, and to obtain both waterproofing and flame resistance at the same time by using an organic phosphor and nitrogen-containing compound and a specific water-repellent compounds in combination.

SOLUTION: A water-repellent compound and organic phosphor and nitrogen-containing compound is stuck to molded natural fiber. The water-repellent compound is a compound having a water-repellent functional group, which is a saturated hydrocarbon group, an aromatic hydrocarbon group, a perfluoroalkyl group, etc. The water-repellent compound further has a hydroxyl group, an amino group, or a carboxyl group. This water-repellent compound includes a solvent base or emulsion base compound; and the solvent base compound is 2,2,2-trifluoroethanol, etc., and the emulsion base compound is perfluoro-n-octanoic acid, etc. The organic phosphor and nitrogen-containing hydrocarbon compound is, e.g. melamine phosphate or melamine cyanurate.

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CLAIMS

[Claim(s)]

[Claim 1] The member for loudspeakers containing the natural fiber cast by the predetermined configuration, and the water-repellent compound adhering to this natural fiber and an organic phosphorus-containing nitrogen-containing compound.

[Claim 2] The member for loudspeakers according to claim 1 in which said water-repellent compound and said organic phosphorus-containing nitrogen-containing compound have adhered to said natural fiber chemically.

[Claim 3] The member for loudspeakers according to claim 1 or 2 in which said water-repellent compound has at least one sort of functional groups chosen from a saturated hydrocarbon radical, an aromatic hydrocarbon radical, a perfluoroalkyl radical, and a fluorine content hydrocarbon group.

[Claim 4] The member for loudspeakers given in either of claims 1-3 in which said water-repellent compound has further at least one sort of functional groups chosen from a hydroxyl group, the amino group, and a carboxyl group.

[Claim 5] Said water-repellent compound is 2, 2, and 2-trifluoro ethanol, hexafluoro isopropanol, 3-amino benzotrifluoride, a pentafluoro aniline, trifluoroacetic acid, and perfluoro. - n - Member for loudspeakers according to claim 4 chosen from an octanoic acid.

[Claim 6] The member for loudspeakers given in either of claims 1-5 said whose organic phosphorus-containing nitrogen-containing compound is melamine phosphate.

[Claim 7] The manufacture approach of the member for loudspeakers which includes the process which heat-treats the natural fiber processed with processing liquid by this casting the process which casts a natural fiber in a predetermined configuration, and the this cast natural fiber with impregnation or the process to coat with the processing liquid containing a water-repellent compound and an organic phosphorus-containing nitrogen-containing compound.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the member for loudspeakers used for various audio equipments, and its manufacture approach. More, this invention does not generate a toxic gas at the time of fume, but relates to the member for loudspeakers with which are simultaneously satisfied of the waterproofness and fire retardancy which are a light weight and high elasticity and were excellent, and its manufacture approach at a detail.

[0002]

[Description of the Prior Art] In recent years, raising thermal resistance and fire retardancy is strongly called for from component parts, such as an electrical machinery and apparatus. It is for preventing the ignition (and fire by that) resulting from the unusual temperature rise by failure of an electrical machinery and apparatus etc.

[0003] The ignition and the fire by the above failures pose a problem also in the loudspeaker. the ignition mechanism of a loudspeaker -- for example, : which is as follows -- amplifier is damaged according to a certain cause, a direct current is impressed to a loudspeaker unit, a voice coil is heated unusually, and a lead line part is disconnected. Consequently, the open-circuit section sparks, ignite from jointing which fixes lead wire, and it burns and spreads on cone paper.

[0004] On the other hand, about the loudspeaker, waterproofness is also an again very important property and the member for loudspeakers which has the outstanding waterproofness is called for. However, the property (namely, fire retardancy) which controls ignition, and waterproofness (or water repellence) are opposite properties, and it is dramatically difficult to satisfy both properties simultaneously.

[0005] The attempt for obtaining the member for loudspeakers which has the outstanding fire retardancy and/or the outstanding waterproofness is indicated by JP,57-50399,B, JP,58-46920,B, and JP,58-1396,A. JP,57-50399,B indicates the diaphragm for loudspeakers which used a water-soluble organic phosphorus series flame retardant and silicone system water repellent. JP,58-46920,B indicates the diaphragm for loudspeakers which mixes the organic system flame retarder, the fixing agent, and water repellent (sizing compound) containing nitrogen, Lynn, and a halogenated compound to a pulp slurry, and comes to mill paper. JP,58-1396,A indicates the diaphragm for loudspeakers which used the organic phosphorus-containing nitrogen-containing compound.

[0006]

[Problem(s) to be Solved by the Invention] However, these techniques have the respectively following troubles.

[0007] Since a water-soluble organic phosphorus series flame retardant is used for a technique given in JP,57-50399,B, if it is going to raise waterproofness, it must add silicone system water repellent so much. Consequently, the weight of a diaphragm increases and reinforcement falls. Since a technique given in JP,58-46920,B mixes an organic system flame retarder, a fixing agent, and water repellent to a pulp slurry and mills paper, its workability is bad. And since a halogenated compound (especially chlorine, a bromine) is used, a toxic gas is generated in a large quantity at the time of combustion, and it has an adverse effect on the body. Furthermore,

sufficient waterproofness is not acquired with this technique. Since an organic phosphorus-containing nitrogen-containing compound is independently used for a technique given in JP,58-1396,A, waterproofness is very low and reinforcement's is inadequate.

[0008] Thus, the member for loudspeakers which is simultaneously satisfied with each above-mentioned periodical of fire retardancy and waterproofness also in the attempt of a publication is not obtained. Therefore, a member for loudspeakers with which are simultaneously satisfied of fire retardancy and waterproofness is desired very strongly.

[0009] This invention does not generate a toxic gas at the time of fume, but are a light weight and high elasticity, and the place which it is made in order to solve the above-mentioned conventional technical problem, and is made into the object has it in offering the member for loudspeakers with which are simultaneously satisfied of the outstanding waterproofness and fire retardancy, and its simple manufacture approach.

[0010]

[Means for Solving the Problem] this invention persons came to complete a header and this invention for the member for loudspeakers which has the outstanding waterproofness and fire retardancy simultaneously being obtained by using combining an organic phosphorus-containing nitrogen-containing compound and a specific water-repellent compound, as a result of examining wholeheartedly the fire retardancy and the waterproofness of the ingredient used for the member for loudspeakers.

[0011] The member for loudspeakers of this invention contains the water-repellent compound adhering to the natural fiber cast by the predetermined configuration and; this natural fiber and an organic phosphorus-containing nitrogen-containing compound, and;

[0012] In a desirable embodiment, the above-mentioned water-repellent compound and the above-mentioned organic phosphorus-containing nitrogen-containing compound have adhered to the above-mentioned natural fiber chemically.

[0013] In a desirable embodiment, the above-mentioned water-repellent compound has at least one sort of functional groups chosen from a saturated hydrocarbon radical, an aromatic hydrocarbon radical, a perfluoroalkyl radical, and a fluorine content hydrocarbon group.

[0014] In a desirable embodiment, the above-mentioned water-repellent compound has further at least one sort of functional groups chosen from a hydroxyl group, the amino group, and a carboxyl group.

[0015] Setting in the desirable embodiment, the above-mentioned water-repellent compound is 2, 2, and 2-trifluoro ethanol, hexafluoro isopropanol, 3-amino benzotrifluoride, a pentafluoro aniline, trifluoroacetic acid, and perfluoro. - It is n. - It is chosen from an octanoic acid.

[0016] In a desirable embodiment, the above-mentioned organic phosphorus-containing nitrogen-containing compound is melamine phosphate.

[0017] This invention offers the manufacture approach of the member for loudspeakers again. The process by which this approach casts a natural fiber in a predetermined configuration; the process which is cast this [;] in the cast this natural fiber with impregnation or the process to coat with the processing liquid containing a water-repellent compound and an organic phosphorus-containing nitrogen-containing compound, and heat-treats the natural fiber processed with processing liquid is included.

[0018]

[Embodiment of the Invention] The member for loudspeakers of this invention contains the water-repellent compound adhering to the natural fiber cast by the predetermined configuration and; this natural fiber and an organic phosphorus-containing nitrogen-containing compound, and;. Especially the natural fiber used in this invention is not limited, but the suitable natural fiber (for example, natural cellulose fiber like wood pulp) of arbitration is used.

[0019] In the member for loudspeakers of this invention, the water-repellent compound and the organic phosphorus-containing nitrogen-containing compound have adhered to the natural fiber by which molding was carried out [above-mentioned]. Typically, a water-repellent compound is a compound which has a water-repellent functional group. as a water-repellent functional group -- a saturated hydrocarbon radical (for example, the shape of a straight chain which has 2-20 carbon atoms and the letter alkyl group of branching -- preferably) The straight chain-like alkyl

group, aromatic hydrocarbon radical which have 3-8 carbon atoms For example, (a phenyl group, benzyl and a naphthyl group), a perfluoroalkyl radical For example, (a perfluoro methyl group, a perfluoro ethyl group, a perfluoro propyl group), A fluorine content hydrocarbon group (for example, 2, 2, and 2-trifluoroethyl radical, a hexafluoro isopropyl group, 3-amino benzotrifluoro radical, perfluoro - n - octyl radical) etc. is mentioned. Especially a desirable water-repellent functional group is a fluorine content hydrocarbon group. Preferably, a water-repellent compound has further a hydroxyl group, an amino group, or a carboxyl group. Such a water-repellent compound contains a solvent system or an emulsion system, and is 2, 2, and 2-trifluoro ethanol, hexafluoro isopropanol, 3-amino benzotrifluoride, a pentafluoro aniline, trifluoroacetic acid, and perfluoro as the example. - It is n. - An octanoic acid etc. is mentioned. Especially a desirable compound is 2, 2, and 2-trifluoro ethanol as a solvent system, and is perfluoro as an emulsion system. - It is n. - It is an octanoic acid.

[0020] As an organic phosphorus-containing nitrogen-containing compound, melamine phosphate and a melamine SHIANU rate are mentioned, for example. Typically in this invention, melamine phosphate is used. Melamine phosphate is prepared by the suitable approach of arbitration.

Drawing 1 is a reaction scheme which shows an example of the preparation approach of melamine phosphate. As shown in drawing 1, a melamine and formaldehyde can be made to be able to react, trimethylolmelamine can be prepared and melamine phosphate can be prepared by making it react with a phosphoric acid in water or water-soluble alcohol.

[0021] Preferably, the above-mentioned water-repellent compound and the organic phosphorus-containing nitrogen-containing compound have adhered to the natural fiber chemically. For example, a natural fiber is cellulose fiber and a water-repellent compound is perfluoro. - n - The case where it is an octanoic acid and an organic phosphorus-containing nitrogen-containing compound is melamine phosphate is explained with reference to drawing 2. When the hydroxyl group (anion part) of cellulose fiber and the ammonium (cation part) in which phosphoric-acid ion dissociated and was formed from melamine phosphate carry out ionic bond, melamine phosphate adheres to cellulose fiber, so that clearly from drawing 2. Furthermore, ammonium and perfluoro of melamine phosphate - n - When octanoic-acid ion carries out ionic bond, cellulose fiber is melamine phosphate and perfluoro. - n - It joins together through an octanoic acid.

[0022] Next, an example of the manufacture approach of the member for loudspeakers of this invention is explained.

[0023] First, a natural fiber is cast in the suitable configuration of arbitration by the suitable approach of arbitration according to an application. For example, in applying this invention to an acoustic radiation plate (diaphragm), beating of the natural fiber is carried out and, subsequently it carries out paper making to a predetermined configuration (for example, a cone mold, a dome mold) using a dip net. Moreover, for example, also when applying this invention to a dust cap, the same molding procedure may be adopted.

[0024] Subsequently, the cast natural fiber is sunk in or coated with the processing liquid containing a water-repellent compound and an organic phosphorus-containing nitrogen-containing compound. The mixing ratio of the water-repellent compound and the organic phosphorus-containing nitrogen-containing compound in processing liquid is 5:95-10:90 preferably. It is a weight ratio. When the rate of a water-repellent compound is less than 5 % of the weight, desired waterproofness is not acquired in many cases. When exceeding 10 % of the weight, other adhesive properties (for example, case of a cone adhesive property with an edge, a voice coil, and a dust cap) and fire retardancy with the member for loudspeakers are insufficient in many cases. The sum density of the water-repellent compound in processing liquid and an organic phosphorus-containing nitrogen-containing compound is 10 % of the weight - 30 % of the weight preferably. The coating weight to the natural fiber of a water-repellent compound and an organic phosphorus-containing nitrogen-containing compound is 10 - 13 % of the weight preferably ten to 20% of the weight to the weight of a natural fiber. The self-extinguishing (fire retardancy) of coating weight of less than 10 % of the weight is insufficient in many cases. If it exceeds 20 % of the weight, the weight of the member for loudspeakers obtained will become heavy too much in many cases. As a solvent used for processing liquid, water, monohydric alcohol (for example, a methanol, ethanol), polyhydric alcohol (for example, ethylene glycol,

propylene glycol), etc. are mentioned. Impregnation or coating is performed by the suitable procedure of arbitration.

[0025] At the end, it is cast, the natural fiber processed with processing liquid is heat-treated, and the member for loudspeakers is obtained. Heat treatment is performed using the suitable means (for example, hot air drying equipment) of arbitration. Heat treatment temperature is 140 °C-160 °C typically. Heat treatment time amount is 1 - 3 minutes typically.

[0026] Hereafter, an operation of this invention is explained.

[0027] Conventionally, although the organic phosphorus-containing nitrogen-containing compound (for example, melamine phosphate) which is a flame retarder was dissociated to melamine ion (cation) and phosphoric-acid ion (anion) in the aqueous solvent, since the dissociated ion drew it electrically and it had them, melamine ion (cation) did not function effectively. Since ionic bond of the melamine ion could not be carried out to the hydroxyl group and validity of a natural fiber (for example, cellulose fiber), more specifically, it was difficult to obtain the member for loudspeakers which has the fire retardancy which could not fully give fire retardancy to cellulose fiber, consequently was excellent. According to this invention, it controls that the ion which the organic phosphorus-containing nitrogen-containing compound dissociated draws each other electrically by using combining an organic phosphorus-containing nitrogen-containing compound and a specific water-repellent compound (2 and 2, small water-repellent compound; for example, perfluoro-n-octanoic acid, of cohesive energy, 2-trifluoro ethanol). Consequently, since the cation of an organic phosphorus-containing nitrogen-containing compound and the hydroxyl group of cellulose fiber form effective and sufficient ionic bond, fire retardancy can fully be given to cellulose fiber (namely, member for loudspeakers). And the water-repellent compound used for this invention serves as an anion in a solvent, and forms the cation part and ionic bond of an organic phosphorus-containing nitrogen-containing compound. Consequently, this water-repellent compound functions also as a cross linking agent which it not only adheres firmly, but combines cellulose fiber with cellulose fiber through an organic phosphorus-containing nitrogen-containing compound. Therefore, it not only gives water repellence (waterproofness) to the member for loudspeakers, but it increases reinforcement (for example, elastic modulus). Furthermore, by the conventional member for loudspeakers, since it does not result in ignition even if it is heated, since the member for loudspeakers of this invention has the fire retardancy which was excellent as mentioned above, even when having become a fire, it ends with fume extent. And a halogen (chlorine, bromine) is not used for this invention as a flame retarder, but the fluorine in a water-repellent compound has small toxicity compared with chlorine or a bromine. Consequently, the member for loudspeakers of this invention does not generate a toxic gas, even when heated unusually.

[0028] As mentioned above, according to this invention, by using combining an organic phosphorus-containing nitrogen-containing compound and a specific water-repellent compound, a toxic gas is not generated at the time of fume, but it is a light weight and high elasticity, and the member for loudspeakers with which are simultaneously satisfied of the outstanding waterproofness and fire retardancy is obtained.

[0029] Furthermore, the member for loudspeakers of this invention is the processing liquid containing the above-mentioned organic phosphorus-containing nitrogen-containing compound and the above-mentioned water-repellent compound, and since it coats and a molding natural fiber is obtained impregnation or by heat-treating, the manufacture process is very simple and low cost.

[0030] This invention may be applied suitable for the member for loudspeakers of various audio equipments (for example, an acoustic radiation plate (diaphragm), a dust cap, an edge, ****).

[0031]

[Example] (Example 1) From North America, it needle-leaf-tree-system-exposed, or non-bleached was carried out, and beating of the kraft pulp was carried out to C.S.F.420ml with the beater, and using the dip net which has a predetermined configuration, paper making was carried out to the cone mold, and it dried. On the other hand, the melamine phosphate dissolved in the methanol and 2, 2, and 2-trifluoro ethanol which dissolved in ethanol were blended at a rate of 10:1 (compound weight ratio), it diluted with the methanol until sum density became 20 % of the

weight, and processing liquid was prepared. The above-mentioned cone paper was sunk in with this processing liquid.

[0032] The cone paper which sank in with processing liquid was heat-treated for 2 minutes by 150 **, and the acoustic radiation plate for loudspeakers (paper cone with an aperture of 16cm) was obtained.

[0033] The following assessment was performed about the obtained acoustic radiation plate. An assessment result is shown in the following table 1.

[0034] 1 In order to evaluate the elastic modulus of an elastic assessment acoustic radiation plate, it is JIS P8209. It applies correspondingly and they are 200 g/m² from cellulose fiber (kraft pulp). The plate sheet was produced and impregnation and the Young's modulus of a sheet heat-treated and obtained were measured using the oscillating Read method on the above-mentioned processing liquid and the above-mentioned processing conditions.

[0035] 2 a fire-resistant assessment U.S. automobile safety standard (FMVSS) — it evaluated according to law (it applies to JIS D1201 correspondingly fundamentally).

[0036] 3 a waterproof assessment profit **** acoustic radiation plate — using — a loudspeaker unit — producing — WhiteNoise with JIS Filter It inputted by rated input 15W. It is a unit tooth back to a shower (flow rate 6 l/min) 120 It showered between parts and was left in the quiescent state after that for 24 hours. Deformation and discoloration of a leak on the loudspeaker front face immediately after shower initiation and exudation, and a loudspeaker were investigated, and f₀ rate of change of 24 hours after was investigated further. When these change was not accepted, and when O.K. and change were accepted in the case where f₀ rate of change is less than 30%, the case where f₀ rate of change exceeded 30% was set to NG.

[0037] 4 The frequency characteristics before and behind the above-mentioned waterproof test in 50cm and input 1W were investigated about an example 1 and the examples 1 and 2 of a comparison on the frequency-characteristics shaft. A result is shown in drawing 3.

[0038]

[A table 1]

	実施例1	実施例2	比較例1	比較例2	比較例3
コーン重量増加率(%)	11.4	11.7	24.0	11.0	3.6
ヤング率(dyn/cm ²)	2.20E+10	2.26E+10	1.05E+10	9.68E+09	2.35E+10
燃焼評価	自己消火性	自己消火性	遅燃性	自己消火性	易燃性
防水評価	OK	OK	OK	NG	OK
f ₀ 変化率(%)	-2.9	-6.2	-15.6	-38.0	-4.4

(Example 2) Perfluoro which dissolved in the melamine phosphate dissolved in water, and propylene glycol - n - The octanoic acid was blended at a rate of 20:1 (compound weight ratio), it diluted with water until sum density became 30 % of the weight, and processing liquid was prepared. The tooth back of the cone paper obtained like the example 1 was coated with this processing liquid with the spin coat method. The following procedures obtained the acoustic radiation plate for loudspeakers like the example 1, and presented the same assessment as an example 1 with it. A result is shown in the above-mentioned table 1.

(Example 1 of a comparison) Except having prepared processing liquid using the water-soluble flame retarder and silicone system water repellent of a publication to JP,57-50399,B, the acoustic radiation plate for loudspeakers was produced like the example 1, and the same assessment as an example 1 was presented. A result is shown in the above-mentioned table 1 and drawing 4.

(Example 2 of a comparison) Except having prepared processing liquid only using the organic phosphorus-containing nitrogen-containing compound of a publication to JP,58-1396,A, the acoustic radiation plate for loudspeakers was produced like the example 1, and the same assessment as an example 1 was presented. A result is shown in the above-mentioned table 1 and drawing 5.

(Example 3 of a comparison) Fluororesin processing liquid (it is 3 % of the weight to

nitrocellulose) was sunk into nitrocellulose (what was diluted with ethyl acetate to 7% of concentration), without performing fireproofing, the acoustic radiation plate for loudspeakers was produced, and the same assessment as an example 1 was presented. A result is shown in the above-mentioned table 1.

[0039] It turns out that the member for loudspeakers of this invention satisfies the outstanding fire retardancy and waterproofness simultaneously so that clearly from a table 1. Furthermore, the members for loudspeakers of this invention are a light weight and high elasticity so that clearly from a table 1. And since there are few toxic gas yields compared with the halogenated compound of others [compound / fluorine content], the member for loudspeakers of this invention also has the advantage of not generating, to the forge fire which has an adverse effect for a toxic gas on the body at the time of fume. Furthermore, the member for loudspeakers of this invention has the distortion small when drawing 3 is compared with drawing 5 of the inside low-pass after a waterproof test compared with the example of a comparison so that clearly.

[0040]

[Effect of the Invention] According to this invention, by using combining an organic phosphorus-containing nitrogen-containing compound and a specific water-repellent compound, a toxic gas is not generated at the time of fume, but it is a light weight and high elasticity, and the member for loudspeakers with which are simultaneously satisfied of the outstanding waterproofness and fire retardancy, and its simple manufacture approach are acquired.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the reaction scheme which shows an example of the preparation approach of melamine phosphate.

[Drawing 2] It is a conceptual diagram for explaining the integrated state of a water-repellent compound and an organic phosphorus-containing nitrogen-containing compound, and cellulose fiber.

[Drawing 3] It is the graph which shows the frequency characteristics of the member for loudspeakers of the example 1 before and behind a waterproof test.

[Drawing 4] It is the graph which shows the frequency characteristics of the diaphragm for loudspeakers of the example 1 of a comparison before and behind a waterproof test.

[Drawing 5] It is the graph which shows the frequency characteristics of the diaphragm for loudspeakers of the example 2 of a comparison before and behind a waterproof test.

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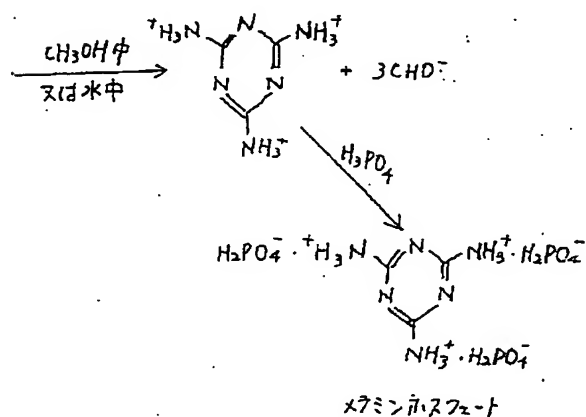
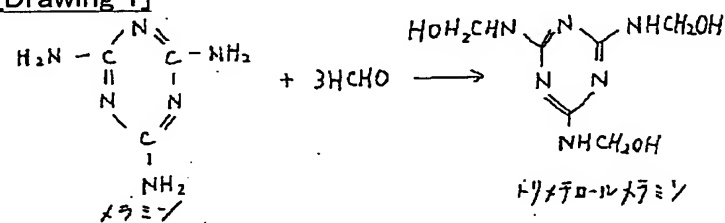
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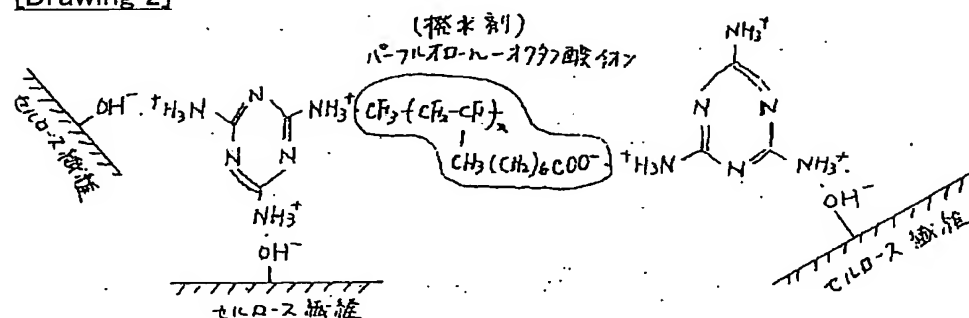
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DRAWINGS

[Drawing 1]

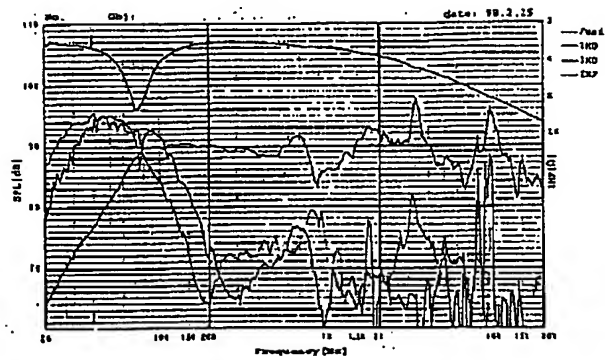


[Drawing 2]

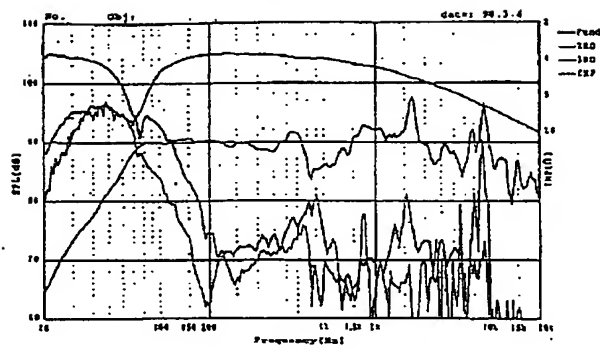


[Drawing 3]

防水試験前

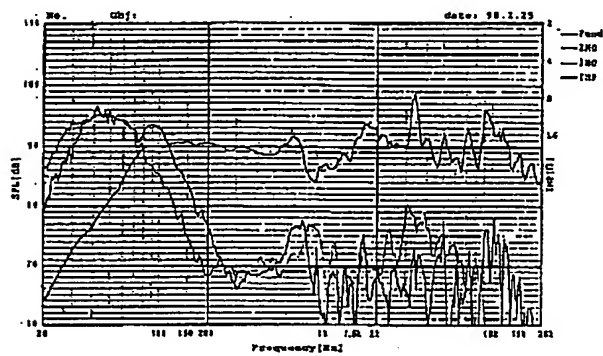


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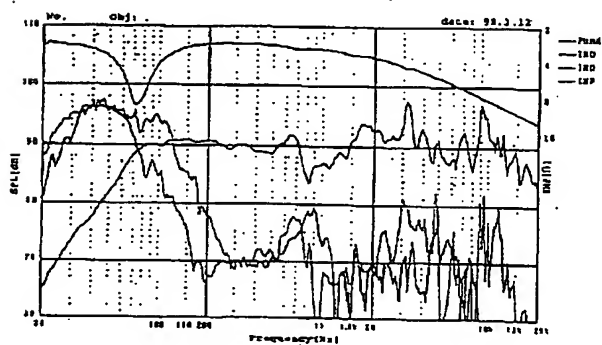


[Drawing 4]

防水試験前

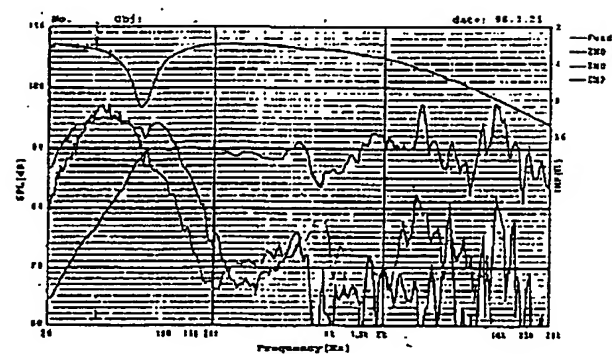


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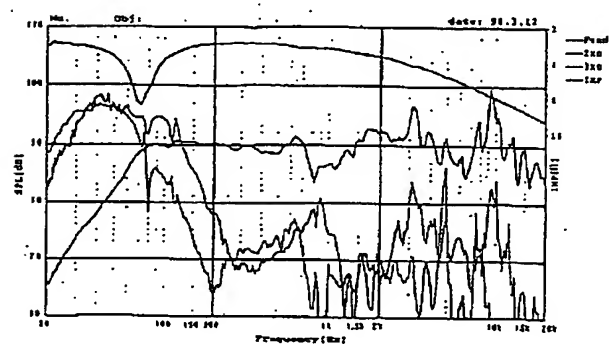


[Drawing 5]

防水試験前



防水試験後



[Translation done.]

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

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JA03

(54) 【発明の名称】 スピーカ用部材およびその製造方法

(57) 【要約】

【課題】 発煙時に有毒ガスを発生せず、軽量かつ高弾性であり、優れた防水性および難燃性を同時に満足するスピーカ用部材を提供すること。

【解決手段】 本発明のスピーカ用部材は、所定の形状に成型されたセルロース繊維と；セルロース繊維に付着した、撥水性化合物および有機含リン含窒素化合物と；を含む。

水性化合物とを組み合わせるにより、優れた防水性と難燃性とを同時に有するスピーカ用部材が得られることを見出し、本発明を完成するに至った。

【0011】本発明のスピーカ用部材は、所定の形状に成型された天然繊維と；該天然繊維に付着した、撥水性化合物および有機リン含窒素化合物と；を含む。

【0012】好ましい実施態様においては、上記撥水性化合物および上記有機リン含窒素化合物は、上記天然繊維に化学的に付着している。

【0013】好ましい実施態様においては、上記撥水性化合物は、飽和炭化水素基、芳香族炭化水素基、パーフルオロアルキル基およびフッ素含有炭化水素基から選択される少なくとも1種の官能基を有する。

【0014】好ましい実施態様においては、上記撥水性化合物は、水酸基、アミノ基およびカルボキシル基から選択される少なくとも1種の官能基をさらに有する。

【0015】好ましい実施態様においては、上記撥水性化合物は、2,2,2-トリフルオロエタノール、ヘキサフルオロイソプロパノール、3-アミノベンゾトリフルオリド、ペンタフルオロアニリン、トリフルオロ酢酸、およびパーフルオロ-n-オクタン酸から選択される。

【0016】好ましい実施態様においては、上記有機リン含窒素化合物は、メラミンホスフェートである。

【0017】本発明はまた、スピーカ用部材の製造方法を提供する。この方法は、天然繊維を所定の形状に成型する工程と；該成型された天然繊維を、撥水性化合物と有機リン含窒素化合物とを含む処理液で含浸またはコーティングする工程と；該成型されそして処理液で処理された天然繊維を熱処理する工程とを含む。

【0018】

【発明の実施の形態】本発明のスピーカ用部材は、所定の形状に成型された天然繊維と；該天然繊維に付着した、撥水性化合物および有機リン含窒素化合物と；を含む。本発明において用いられる天然繊維は特に限定されず、任意の適切な天然繊維（例えば、木材パルプのような天然セルロース繊維）が用いられる。

【0019】本発明のスピーカ用部材においては、上記成型された天然繊維に、撥水性化合物と有機リン含窒素化合物とが付着している。撥水性化合物は、代表的には、撥水性官能基を有する化合物である。撥水性官能基としては、飽和炭化水素基（例えば、2～20個の炭素原子を有する直鎖状または分岐状アルキル基、好ましくは、3～8個の炭素原子を有する直鎖状アルキル基）、芳香族炭化水素基（例えば、フェニル基、ベンジル基、ナフチル基）、パーフルオロアルキル基（例えば、パーフルオロメチル基、パーフルオロエチル基、パーフルオロプロピル基）、フッ素含有炭化水素基（例えば、2,2,2-トリフルオロエチル基、ヘキサフルオロイソプロピル基、3-アミノベンゾトリフルオロ基、パーフルオロ-n-オクチル基）などが挙げられる。特に好ましい撥水性官

能基は、フッ素含有炭化水素基である。好ましくは、撥水性化合物は、水酸基、アミノ基またはカルボキシル基をさらに有する。このような撥水性化合物は、溶剤系またはエマルジョン系を含み、その具体例としては、2,2,2-トリフルオロエタノール、ヘキサフルオロイソプロパノール、3-アミノベンゾトリフルオリド、ペンタフルオロアニリン、トリフルオロ酢酸、パーフルオロ-n-オクタン酸などが挙げられる。特に好ましい化合物は、溶剤系としては2,2,2-トリフルオロエタノールであり、エマルジョン系としてはパーフルオロ-n-オクタン酸である。

【0020】有機リン含窒素化合物としては、例えば、メラミンホスフェート、メラミンシアヌレートが挙げられる。本発明においては、代表的には、メラミンホスフェートが用いられる。メラミンホスフェートは、任意の適切な方法で調製される。図1は、メラミンホスフェートの調製方法の一例を示す反応スキームである。図1に示すように、メラミンとホルムアルデヒドとを反応させてトリメチロールメラミンを調製し、水または水溶性アルコール中でリン酸と反応させることによりメラミンホスフェートを調製することができる。

【0021】好ましくは、上記撥水性化合物および有機リン含窒素化合物は、天然繊維に化学的に付着している。例えば、天然繊維がセルロース繊維であり撥水性化合物がパーフルオロ-n-オクタン酸であり有機リン含窒素化合物がメラミンホスフェートである場合について、図2を参照して説明する。図2から明らかなように、セルロース繊維の水酸基（アニオン部分）と、メラミンホスフェートからリン酸イオンが解離して形成されたアンモニウム基（カチオン部分）とがイオン結合することにより、メラミンホスフェートがセルロース繊維に付着する。さらに、メラミンホスフェートのアンモニウム基とパーフルオロ-n-オクタン酸イオンとがイオン結合することにより、セルロース繊維同士がメラミンホスフェートおよびパーフルオロ-n-オクタン酸を介して結合する。

【0022】次に、本発明のスピーカ用部材の製造方法の一例について説明する。

【0023】まず、天然繊維を、用途に応じて、任意の適切な方法により任意の適切な形状に成型する。例えば、本発明を音響放射板（振動板）に適用する場合には、天然繊維を叩解し、次いで、抄網を用いて所定の形状（例えば、コーン型、ドーム型）に抄紙する。また例えば、本発明をダストキャップに適用する場合にも、同様の成型手順が採用され得る。

【0024】次いで、成型された天然繊維を、撥水性化合物と有機リン含窒素化合物とを含む処理液で含浸またはコーティングする。処理液における撥水性化合物と有機リン含窒素化合物との混合比は、好ましくは5:95～10:90の重量比である。撥水性化合物の割合が5重量

シャワー開始直後のスピーカ表面への水漏れおよびしみ出し、スピーカの変形および変色を調べ、さらに、24時間後のf0変化率を調べた。これらの変化が認められない場合かつf0変化率が30%未満である場合をOK、変化が認められた場合またはf0変化率が30%を超える場合をNGとした。

【0037】4 周波数特性

軸上50cm、入力1Wにおける上記防水試験前後の周波数特性を実施例1、比較例1および2について調べた。結果を図3に示す。

【0038】

【表1】

	実施例1	実施例2	比較例1	比較例2	比較例3
コーン重量増加率(%)	11.4	11.7	24.0	11.0	3.6
ヤング率(dyn/cm ²)	2.20E+10	2.26E+10	1.05E+10	9.68E+09	2.35E+10
燃焼評価	自己消火性	自己消火性	遅燃性	自己消火性	易燃性
防水評価	OK	OK	OK	NG	OK
f0変化率(%)	-2.9	-6.2	-15.6	-38.0	-4.4

(実施例2) 水に溶解したメラミンホスフェートとプロピレングリコールに溶解したパーフルオロ-n-オクタン酸とを20:1(化合物重量比)の割合でブレンドし、合計濃度が30重量%となるまで水で希釈して、処理液を調製した。実施例1と同様にして得られたコーン紙の背面に、スピンコート法によりこの処理液をコーティングした。以下の手順は実施例1と同様にしてスピーカ用音響放射板を得、実施例1と同様の評価に供した。結果を上記表1に示す。

(比較例1) 特公昭57-50399号公報に記載の水溶性難燃剤とシリコン系撥水剤とを用いて処理液を調製したこと以外は実施例1と同様にしてスピーカ用音響放射板を作製し、実施例1と同様の評価に供した。結果を上記表1および図4に示す。

(比較例2) 特開昭58-1396号公報に記載の有機含リン含窒素化合物のみを用いて処理液を調製したこと以外は実施例1と同様にしてスピーカ用音響放射板を作製し、実施例1と同様の評価に供した。結果を上記表1および図5に示す。

(比較例3) 難燃処理を施さずに硝化綿(酢酸エチルで濃度7%に希釈したもの)にフッ素樹脂処理液(硝化綿に対して3重量%)を含浸してスピーカ用音響放射板を作製し、実施例1と同様の評価に供した。結果を上記表1に示す。

【0039】表1から明らかなように、本発明のスピーカ用部材は、優れた難燃性と防水性とを同時に満足することがわかる。さらに、表1から明らかなように、本発

明のスピーカ用部材は、軽量かつ高弾性である。しかも、本発明のスピーカ用部材は、フッ素含有化合物が他のハロゲン化合物に比べて有毒ガス発生量が少ないので、発煙時に有毒ガスを人体に悪影響を及ぼすほどには発生しないという利点も有する。さらに、図3と図5とを比較すると明らかなように、本発明のスピーカ用部材は、比較例に比べて防水試験後の中低域の歪みが小さい。

【0040】

【発明の効果】本発明によれば、有機含リン含窒素化合物と特定の撥水性化合物とを組み合わせることで、発煙時に有毒ガスを発生せず、軽量かつ高弾性であり、優れた防水性および難燃性を同時に満足するスピーカ用部材およびその簡便な製造方法が得られる。

【図面の簡単な説明】

【図1】メラミンホスフェートの調製方法の一例を示す反応スキームである。

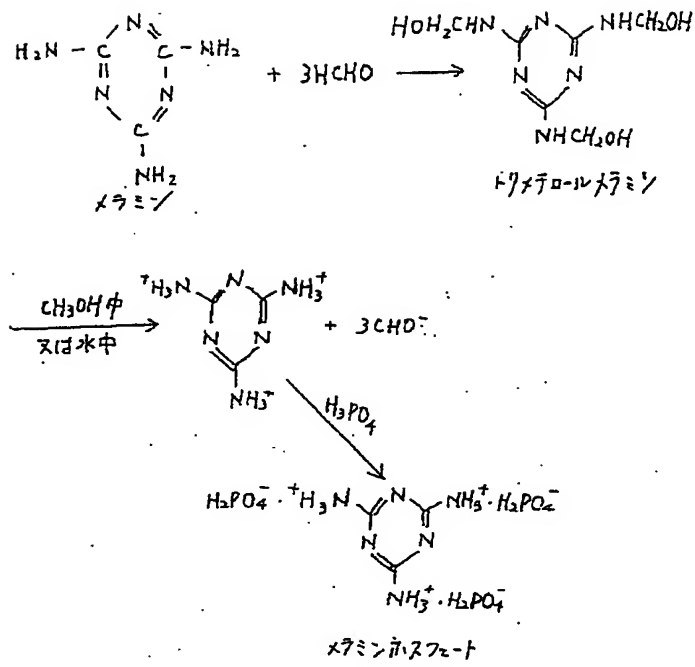
【図2】撥水性化合物および有機含リン含窒素化合物とセルロース繊維との結合状態を説明するための概念図である。

【図3】防水試験前後における実施例1のスピーカ用部材の周波数特性を示すグラフである。

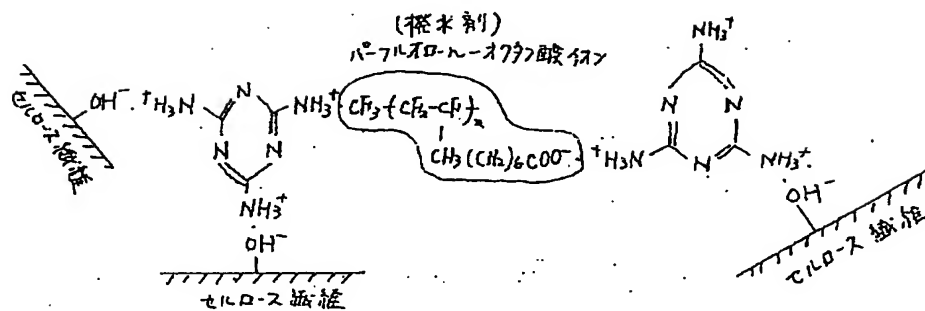
【図4】防水試験前後における比較例1のスピーカ用振動板の周波数特性を示すグラフである。

【図5】防水試験前後における比較例2のスピーカ用振動板の周波数特性を示すグラフである。

【図 1】

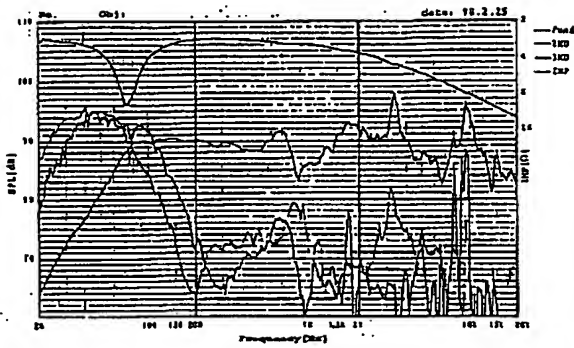


【図 2】



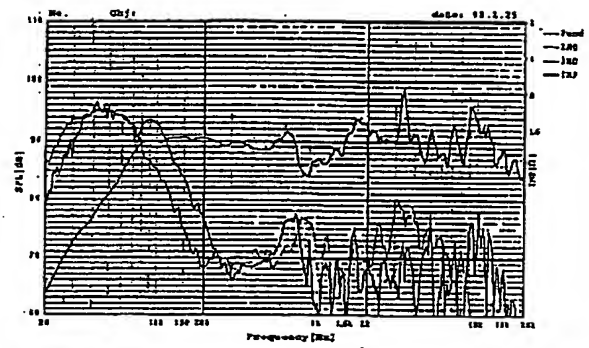
【図3】

防水試験前

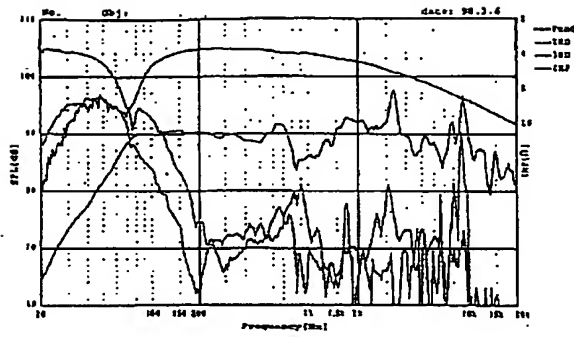


【図4】

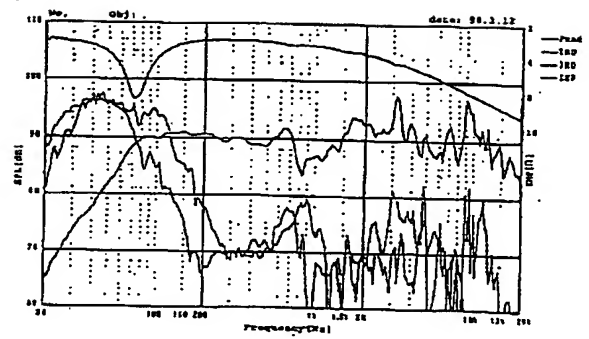
防水試験前



防水試験後

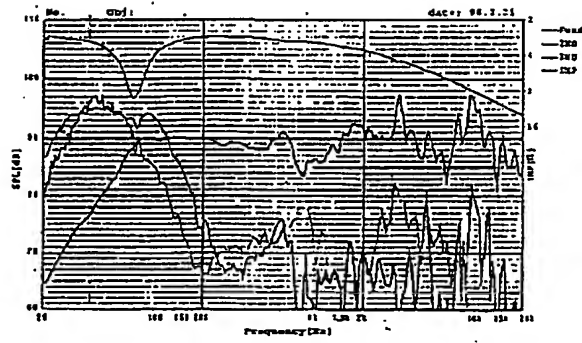


防水試験後



【図5】

防水試験前



防水試験後

